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Evidence for Pore Water Composition Controlling Carbonate Morphology in Concrete and the Further Effect of Gamma Radiation

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Abstract

Radiation, heat and carbonation can all affect the performance of concrete structures. This study applies either a 1.5 MGy gamma radiation dose or thermal treatment at 60 °C, followed by an accelerated carbonation period. In comparison to a control sample, irradiation and heat treatment lead to an increase in the carbonation depth which correlates with an increase in crack depth induced by restrained drying-induced shrinkage. When compared to thermally treated samples, there is greater variability in the crack depth of irradiated samples which we ascribe to a radiation-induced change in the mechanical properties of the cement paste. X-ray diffraction is used to identify the calcium carbonate polymorphs that form as result of carbonation. The dominant phase in the control sample is vaterite whereas the dominant phase in both the irradiated and thermally treated samples is calcite. Gamma

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irradiation leads to a greater calcite:vaterite ratio than thermal treatment.
The sequential application of gamma radiation/heat treatment followed by
a carbonation period rules out radiolytically produced calcium peroxide oc-
tahydrate as the cause of the polymorph switch as it is too short-lived. A
new mechanism is hypothesised, where elemental substitution into the cal-
cium carbonate lattice results in deformation and so alters the morphology
of the calcium carbonate, leading to the formation of a different polymorph.

Keywords: Gamma Radiation, Accelerated Carbonation, Cement,
Concrete, Nuclear

1 1. Motivation

2 Cement and concrete are widely used in the nuclear industry for a variety
3 of purposes, with structural uses being very common. A key consideration
4 for structural uses is the long operational timespan, typically on the order
5 of decades, where they are exposed to multiple degradation pathways, such
6 as radiation, erosion and thermal dehydration. Since these structures pro-
7 vide safety functions [1] it is important to understand how these structures
8 age. Carbonation, the process of CO₂ gas from the atmosphere reacting with
9 calcium containing phases present in cement [2], can occur over these long
10 operational timescales. The effects of carbonation are well documented, in-
11 cluding changes in porosity, cracking and pH [3]. Carbonation is normally
12 associated with an increase in compressive strength [4, 5], however it has
13 been shown to decrease the compressive strength in some situations [6]. The
14 drop in pH can lead to the corrosion of steel re-bar, which is sometimes
15 present in structural concrete, and consequently lead to cracking in the con-

crete structure and spalling in some cases [3, 7, 8]. Studies have shown that irradiation can modify the carbonation process, leading to a different calcium carbonate polymorph being formed due to thermal dehydration, as well as an increase in the total amount of carbonated phase [9, 10]. The modifying effects of radiation on carbonation, and hence on compressive strength, are not yet fully understood and, since various studies have used cement of specific compositions [9, 10, 11], appear to be affected by the composition of the cement.

It has long been reported that radiation affects the properties of cement and concrete structures [12] and that changes in compressive strength as a result of irradiation depend on the composition of the cement. While many studies have focused on the combined effect of neutron and gamma irradiation, applicable to nuclear power plants, there are only a few studies on the effect of gamma radiation alone, which is relevant to facilities that store nuclear materials. A dose of 5×10^5 Gy has been shown to cause a 10 % drop in the compressive strength of ordinary Portland cements (OPC) cements [13, 14], with a larger change observed when a lower dose rate was applied [14]. Whilst gamma radiation typically causes the compressive strength to decrease, carbonation normally results in an increase [2]. In the case of early aged blast furnace slag (BFS) blended cements, Mobasher et al. [15] found that compressive strength increased after irradiation, accompanied by increased porosity. Craeye et al. [16] found that compressive strength was reduced when samples were exposed to gamma radiation at an early age, with the addition of BFS increasing this behaviour. Tajuelo Rodriguez et al. [17] examined synthesised calcium-silicate-hydrate samples subjected up to

41 0.784 MGy over 12 months, and found little change in the chemical-physio
42 properties of the material. Interestingly, no interlayer water was lost which is
43 believed to be the main reason for lack of change in the mechanical properties.
44 There have been several studies measuring the radiolytic production of H_2
45 in cementitious systems, which have highlighted radiolytic processes can be
46 affected by numerous variables, such as water content, phases present and
47 dose rate. [18, 19, 20]

48 When simultaneously exposed to gamma radiation and a carbonating at-
49 mosphere, the degree of carbonation in a hardened cement paste increases
50 [10, 11]. All of the studies that have examined the effects of carbonation and
51 gamma irradiation have been conducted under natural carbonation condi-
52 tions, resulting in experiments several months long.

53 Vodák et al. [10] found that irradiation resulted in a decrease in the mass
54 of cement paste, and suggested that this mass loss was due to dehydration
55 caused by radiolytic breakdown of the pore water. Bouniol and Bjergbakke
56 [21] found that unstable calcium octahydrate peroxide can be formed in the
57 cement pore water during irradiation, however, in the case of very low dose
58 rates there needs to be a minimum amount of hydrogen peroxide present
59 in solution before the calcium octahydrate peroxide can form. Higher dose
60 rates were shown to increase the maximum amount of the peroxide formed.
61 It has been suggested that this unstable calcium peroxide can lead to in-
62 creased carbonation in a radiation field [9, 13]. Maruyama et al. [9] reported
63 that samples simultaneously exposed to gamma radiation and carbonation
64 formed vaterite and aragonite predominantly, whereas calcite was dominant
65 under solely carbonating atmospheres. Vaterite, aragonite and calcite are

66 metastable polymorphs of calcium carbonate (CaCO_3), that possess differ-
67 ent morphologies, [22, 23, 24, 25, 26].

68 In carbonation experiments, it is common to use accelerated testing,
69 where the volume of CO_2 in the air around the sample is increased. The
70 maximum amount of CO_2 which is representative of natural carbonation is
71 still debated. For OPC, Castellote et al. [27] showed that 3 % CO_2 atmo-
72 sphere produced microstructure similar to natural carbonation, whereas at
73 10 % CO_2 there were obvious differences, such as the disappearance of the
74 C-S-H gel. Auroy et al. [28] also demonstrated that 3 % CO_2 was representa-
75 tive of natural carbonation for pure OPC systems. When the cement system
76 contained both BFS and fly ash (FA) there was a larger discrepancy between
77 accelerated and natural carbonation results. Furthermore, Auroy et al. [28]
78 found that different phases present in hardened cement pastes (HCP) result
79 in different carbonation polymorphs.

80 Calcium carbonate polymorphs are well researched in other fields, in par-
81 ticular their precipitation in seawater conditions. It is well established that
82 pure calcite is the most stable polymorph and vaterite is the least stable
83 [22] due to the crystal structures of the polymorph, however the inclusions
84 of various ions can affect the stability. For example, Mg can substitute
85 into the calcite lattice, destabilising the structure with the inclusion of more
86 Mg [23, 24]. As a result of this destabilisation, aragonite becomes more
87 favourable. Similarly Bots et al. [23] found that S can substitute into calcite
88 (as SO_4) and replace CO_3 , causing an anisotropic change in the unit cell
89 parameters. However, S substitution did not significantly affect the crys-
90 tal cell parameters of aragonite or vaterite, meaning these polymorphs were

91 more apparent when S was present during synthesis. Being the least sta-
92 ble polymorph, Rodriguez-Blanco et al. [25] demonstrated that vaterite can
93 transform to calcite under ambient conditions, resulting in a defected calcite
94 morphology. Both pH and the presence of Mg have been shown to alter the
95 pathway to forming calcite, where neutral pH or the presence of Mg led to the
96 formation of calcite directly from amorphous calcium carbonate [26]. Hsiao
97 et al. [29] have examined the effects of Ar^+ ion irradiation on calcite, showing
98 an insensitivity to radiation, via both experimental and modelling methods.
99 Whilst gamma radiation is significantly different to ion irradiation [30, 31],
100 Hsiao et al. [29] findings would imply that radiation damage directly to the
101 calcite phase would not affect the type of polymorph. Therefore, an indirect
102 effect of irradiation is more likely to be the cause of the polymorph switch.

103 Carbonation alters the porosity of cementitious materials and directly
104 influences the compressive strength of the material. The different carbonate
105 polymorphs have different molar volumes, which leads to different degrees of
106 porosity and so may alter the compressive strength accordingly. This paper
107 seeks to better understand the mechanism that leads to a given calcium
108 carbonate polymorph being formed as a result of gamma irradiation alongside
109 carbonation, utilising a new methodology. The literature has shown that
110 thermal dehydration affects the carbonate polymorph formed [9] and so this
111 paper investigates dehydration and any associated cracking so that the extent
112 of CO_2 penetration into the cement, and associated depth of carbonation, can
113 be understood.

114 2. Methodology

115 2.1. Sample Preparation

116 The composition of our samples is based on a specification provided by
117 Sellafield Ltd (equivalent to BS EN 197-1 CEM I 42,5N [32]). Ordinary
118 Portland cement (OPC) was used to meet Sellafield Ltd specification and
119 fly-ash (FA), category EN450-NB from Drax [33], was used. A mix ratio of
120 3:2 OPC:FA was used with a water to solids ratio of 0.5. Characterisation
121 of the raw powders was carried out via SEM and EDS which are provided in
122 Figure 1 and Table 1.

Figure 1: SEM images taken of the FA and OPC powders, using a secondary electron detector

123 The above constituents were combined in planetary mixer for 5 minutes
124 and the resultant paste was then decanted into 40 mm cubic moulds, covered
125 with clingfilm and left overnight. After removing from the moulds, samples
126 were placed into a water bath filled with a lime saturated solution to cure for 6
127 weeks. The temperature was set to 20 °C which fluctuated by approximately

Table 1: Averaged EDS results for the elemental composition of the FA and OPC powders. 30 measurements were taken for each powder. Values provided are wt %

	O	Al	Si	K
FA	51.3 $\pm$ 6.3	11.9 $\pm$ 4.6	22.5 $\pm$ 8.0	2.3 $\pm$ 1.2
OPC	32.67 $\pm$ 13.6	2.1 $\pm$ 2.8	7.5 $\pm$ 3.9	-
	Fe	Ca	Cu	Mg
FA	6.1 $\pm$ 11.5	-	-	-
OPC	4.2 $\pm$ 6.3	49.9 $\pm$ 13.3	0.5 $\pm$ 0.3	0.50 $\pm$ 0.31

128 2 °C over this period. In total, 9 samples were produced from this mixture.
 129 As a result the samples were 42 days old a the start of the experiment.

130 2.2. Irradiation and Heat Treatment

131 After being removed from the water bath the samples were patted dry
 132 and left on a bench top for an hour to remove any excess moisture. 5 faces
 133 of the samples were coated with self-adhesive aluminium tape to restrict car-
 134 bonation to 1 direction. The masses were recorded before and after applying
 135 the aluminium tape.

136 Irradiation was carried out at the Dalton Cumbrian Facility [34] using a
 137 self shielded ^{60}Co gamma irradiator. The exposed face of 3 samples was
 138 placed so it was closest to the radiation source. The irradiation lasted
 139 65.5 hours, with a dose rate of 385 Gy/min, giving a total dose of 1.5 MGy.
 140 The samples were stacked on top of each other, meaning each received a
 141 slightly different dose. This variation is within 5%.

142 Due to the lead shielding surrounding the sample chamber of the gamma
 143 irradiator [34], the temperature rises during the irradiation, reaching approx-

144 imately 60 °C. To distinguish the effects of gamma irradiation from heating,
145 3 samples were placed into a oven set at 60 °C during the irradiation. Addi-
146 tionally, 3 control samples were set aside in the lab during this time. This
147 elevated temperature means some cracking was expected due to restrained
148 drying shrinkage [35, 36]. It should be noted that all the samples were ex-
149 posed to atmospheric conditions during this period. Immediately after this
150 treatment period, the mass of each sample was recorded before being placed
151 into a carbonation chamber. Images were also taken of the exposed face,
152 using a DSLR camera.

153 *2.3. Carbonation*

154 A simple carbonation chamber was constructed for this study, with a
155 schematic given below in Figure 2. A feedback loop utilising a solenoid valve
156 connected to a gas bottle is used to provide a 5 % CO₂ atmosphere over the
157 two week carbonation period. The CO₂ level dropped to 4.3 % over the final
158 10 hours as the supply from the gas bottle was depleted.

159 A K-33 BLG CO₂ Sensor was used to detect the carbon dioxide level,
160 as well as recording relative humidity and temperature. A saturated salts
161 solution of sodium nitrite provided a relative humidity of around 75 %, higher
162 than the expected 67 % selected to maximise the accelerated carbonation
163 process [37]. A final mass reading was taken as soon as the samples were
164 removed from the carbonation chamber. Similarly, more images were taken
165 of the exposed face so that the evolution of the cracks could be characterised.

Figure 2: Schematic of the carbonation chamber built for this study

2.4. Analysis

Samples were sliced up for analysis, as Figure 3 demonstrates. The slices from the top half were used for analysis via pH indicator spraying, XRD mapping techniques, and SEM (discussed in Section's 2.4.2- 2.4.4). The bottom half of each sample was cut into slices perpendicular to the exposed face. RS pro vernier calipers were used to keep the slice size consistent at 3 mm. These slices were ground with an agate mortar and pestle and sieved to between 300-500 μm . Samples were stored in sealed plastic bags until analysis, with the time between grinding to a powder and being analysed kept to a minimum, ready for leaching of pore water and subsequent analysis of the leachate by ICP-AES.

2.4.1. Characterisation of Cracking

The obtained images of the exposed face were loaded into imaging software, whereby they were converted to 8-bit greyscale images. These were then manually thresholded using the histogram to highlight the cracking. A

Figure 3: Schematic of the method used to slice samples for analysis. Mapping slices indicates slices used for the mapping XRD, phenolphthalein indicator and SEM, whereas powder slices were the slices used for ICP-AES analysis.

distance calibration allowed a 30 mm square crop of the central section to be taken, avoiding any aluminium tape on the edges which would interfere with the subsequent analysis. This crop was then converted to a binary image and noise was manually cleaned up using a circular selection and fill tool. Speckling on the surface prevented automatic noise reduction software from working, due to the speckles overlapping with the cracks on the histogram during the thresholding process. In the case of the heated samples after treatment phase, this approach was significantly better than the automatic noise reduction, however, still resulted in cracks that look wider than they are. Supplementary material are provided, which show the process as 3 steps for the all the samples in Figure 5.

2.4.2. Phenolphthalein Indicator

With the mapping slices, phenolphthalein indicator was sprayed onto one side of a mapping slice. Digital image correlation was used to obtain multiple readings of the carbonation depth. Pictures were taken with a Nikon D3100 under ambient lighting, with the length of the sample obtained via vernier calipers for image calibration. Image J was used for the analysis, with a

script provided by Prof. Helmut Glünder, allowing a measurement to be taken every 10 pixels over a manually set range for each sample. The colour change from the phenolphthalein indicator was used as a guide when cutting the sample into edge and centre pieces for further analysis: centre pieces did not exhibit a colour change and so were considered to be uncarbonated. This approach allowed comparison of carbonated material to uncarbonated material and so negates the need to analyse samples after treatment but before carbonation.

2.4.3. Mapping XRD

The mapping XRD scans were carried out from $16 - 60^\circ 2\theta$ range, using a $0.116^\circ 2\theta$ step size. Due to low counting rates each scan took 3 hours. Scans were taken from the exposed edge inwards, with 0.42 mm increments taken over a range of 12 mm for the heat treated and irradiated samples and 9 mm for the control samples. These ranges were guided by the carbonation depths determined by the phenolphthalein indicator. For each sample, total run time was approximately 90 hours. A custom 3D printed cell made by Dr. J. Warren (Senior Experimental Officer, University of Manchester), was used to flow nitrogen over the sample throughout the run, preventing carbonation.

2.4.4. Scanning Electron Microscope

A Scanning Electron Microscope (SEM) was used to examine the morphology of carbonation products. A slice of sample was polished using successive grits up to 2000 grit paper, for 2 minutes each time.

After polishing the sample was rinsed and dried overnight at 30°C under vacuum. After drying the sample was gold coated for 15 seconds to avoid the

222 sample charging.

223 *2.4.5. Analysis of Powdered Samples*

224 To understand the pore water chemistry, slices taken from the edge and
225 middle of each carbonated sample, which were subsequently powdered, were
226 placed in vials with de-ionised water ($18.2\text{ M}\Omega$) in a 1:10 mass ratio, capped,
227 and stored for 28 days at room temperature. The leachate was then sampled
228 and passed through a $0.45\text{ }\mu\text{m}$ filter prior to analysis via inductively coupled
229 plasma atomic emission spectroscopy (ICP-AES).

230 **3. Results**

231 *3.1. Extent of Carbonation*

232 Prior to carbonation, mass loss was observed in both the heat treated
233 and irradiated samples, as shown in Figure 4. Since the degree of mass loss
234 was within error between the irradiated and heated samples, evaporation
235 of loosely bound pore water is thought to be the cause of this. Both the
236 heated and irradiated samples gained significant mass after the carbonation
237 stage compared to the control sample. Given that calcite is denser than
238 the C-S-H phase, some of this mass gain could be from carbonation and,
239 given the relative humidity in the carbonation chamber, some could be from
240 re-adsorption of water.

241 The evaporation of water occurs from the exposed surface of the sample
242 during the treatment phase, effectively drying out the exposed face. This
243 has led to restrained drying shrinkage-induced cracking [35, 36], shown in
244 Figure 5. Cracking only occurs where strain is introduced and the extent of

Figure 4: Mass measurements at each stage of the experiment. Each bar is an average of 3 samples

245 this process is affected by several factors, such as relative humidity, temper-
 246 ature and drying extent. Our results demonstrated a more developed crack
 247 network in the irradiated samples compared to the heat control samples.
 248 Greater cracking should lead to more penetration of CO_2 and so increase the
 249 carbonation depth.

250 Carbonation depths were obtained from cement samples sprayed with
 251 phenolphthalein solution. As the ingress of the carbonation phase was not
 252 completely even, histograms are the best representation of these data sets.
 253 These are shown in Figure 6, where both the histogram and a kernel density
 254 estimation (KDE) are plotted.

255 As expected from the mass loss data in Figure 4 and the cracking observed
 256 in Figure 5, both the irradiated and heated samples show an increase in the
 257 carbonation depth. The mean values are provided in Table 2, which demon-
 258 strates that heating or irradiating samples prior to carbonation effectively

Figure 5: Examples of the crack analysis. Note the darker, wider cracking observed on 5b is an artefact of the noise reduction due to speckled sample surface. Cracking was not observed on the control sample after the treatment phase.

259 doubled the depth of carbonation ingress. Both Figure 6 and Table 2 show
 260 that the irradiated sample had a significantly wider spread of carbonation
 261 depth compared to the other sample groups. Figure 7 shows that cracks line
 262 up with indents in the phenolphthalein and we surmise that, since cracks
 263 would increase the diffusion of CO_2 into the cement, the variation in carbon-
 264 ation depths correlates with various crack depths

Figure 6: Histograms of the carbonation depth measurements obtained in Image J. Kernel density estimation (lines in Figure 6d) plots are to guide the eye.

Table 2: Mean distances from the carbonation depth measurements.

Sample	Mean (mm)	Deviation (mm)
Irradiated Carbonated	6.14	2.24
Heated carbonated	6.18	1.35
Carbonated	3.02	1.24

265 3.2. Carbonation Phases

266 The XRD data are provided in Figure 8 using heatmaps to clearly present
 267 the multiple XRD spectra that were collected at intervals along sliced sam-

Figure 7: Images of slices sprayed with phenolphthalein showing the extent of cracking in the carbonated regions.

268 ples. Figure 8a shows the dominant carbonation polymorph formed in the
 269 control sample to be vaterite, with no appreciable proportion of calcite ob-
 270 served. Both the irradiated and heat treated samples also show vaterite
 271 formation, however, calcite is also formed in considerable quantities. The
 272 observed quartz in Figure 8 is due to the fly-ash.

273 There are subtle differences between the heatmaps generated for the ir-
 274 radiated and heat treated samples; the calcite:vaterite ratio is significantly
 275 larger in the irradiated sample, compared to the heat treated sample. These
 276 ratios are provided in Figure 9, which compares the area of the vaterite peak
 277 at $27.1\ 2\theta$ to the area of the calcite peak at $29.4\ 2\theta$.

278 3.3. Pore Water Chemistry and SEM imaging of carbonate morphology

279 Figure 10 shows an example of the carbonation products found in the
 280 irradiated sample. Energy dispersive x-ray spectroscopy was used to iden-
 281 tify phases with substantial carbon content, typical of carbonation products.
 282 Figure 10 is believed to be calcite as the morphology appears to be somewhat
 283 cubic rather than the spherical morphology of vaterite. The morphology of
 284 the calcite is imperfect compared to the cubic morphology observed when
 285 calcium carbonate is synthesised from solution [22]. Imperfect morphology

Figure 8: Heatmaps showing evolution of the carbonation phase into the sample, where the bottom is the carbonated edge. P = portlandite, Q = quartz, V = vaterite, A = aragonite, C = calcite, C-S-H = calcium-silicate-hydrate

indicates the material structure is defected, which could be caused by elements from the cement matrix interacting with the carbonate. Analysis of the pore water leachate provides further insight into this by identifying elements present in the edge and middle of the samples.

Figure 11 shows some interesting trends, in particular for the elements Ca, Na, K and S. Here, leachate taken from the middle of the samples corresponds to uncarbonated cement while samples from the edge were found to be carbonated. The data for Si and Mg suggests that they appear in the pore water only in small concentrations and do not seem to be affected by

Figure 9: Plot comparing the calcite to vaterite ratio from Figure 8

carbonation, heat treatment or irradiation.

Figure 10: SEM image of the carbonated area of the irradiated sample, showing what is thought to be a calcite crystal, as determined by EDX

Figure 11: ICP-AES data for leachate taken from the edge and middle of the different samples. Error bars are the standard deviation from 3 repeats of same leachate

295

296 Leachate collected from the middle of the irradiated and heat treated
 297 samples has a lower Ca concentration when compared to the control samples
 298 suggesting that irradiation and heating prior to carbonation lead to the for-
 299 mation of Ca-bearing mineral phases. Examining the leachate from all 3 edge

300 samples shows an increase in the Ca content, meaning that some Ca-bearing
 301 phases have dissolved during the carbonation period. Irradiation/heating
 302 appear to increase this effect given the larger relative increase in Ca content
 303 from centre to edge. A decrease is observed in the Na and K content of the
 304 leachate from the edge samples compared to the centre samples, indicating
 305 these ions may have been incorporated into the carbonate phase at the ex-
 306 pense of Ca, which would also contribute to the increase in Ca content at
 307 the edges.

308 Gamma irradiation and/or heating has resulted in an increase in the
 309 concentration of S in the leachate from the middle of the samples, suggesting
 310 that it was released into solution prior to carbonation. This suggests that
 311 both irradiation and heating leads to dissolution of S-containing phases prior
 312 to carbonation. Data collected from leachate from the edge of the samples
 313 shows that the concentration of S in the pore water increases in all three
 314 samples compared to the middle; this is due to the carbonation of ettringite
 315 [28, 38, 39].

316 4. Discussion

317 4.1. Carbonation Depth

318 The data provided in Section 3.1 is in good agreement with Vodák et al.
 319 [10] and Bar-Nes et al. [11]: irradiation led to an increase in the carbonation
 320 depth. In our samples, the mean carbonation depth in the control sample
 321 was 3.02 mm compared to 6.18 mm in the irradiated samples. Thermal dehy-
 322 dration, indicated by mass loss of $3.71 \pm 0.47\%$ and $3.30 \pm 0.11\%$ after the
 323 treatment phase for both the irradiated and heat treated samples respectively

(Figure 4), allowed CO_2 to diffuse in to the cement. This CO_2 diffusion was further enhanced by the appearance of cracks, in both the irradiated and heat treated samples after the treatment phase (Figure 5). Similar mass loss observed between the irradiated and heated samples after treatment indicates a similar amount of pore water removal in these samples. The 2.51 – 2.71% mass increase after carbonation for the irradiated and heat treated samples is due to either the carbonation process or water re-absorbing into the samples. Future work could identify the cause by re-running the experiment, but instead exposing the samples to normal atmosphere at the same relative humidity as the carbonation run. Thermogravimetric analysis could then be used to quantify the phase contents.

The more extensive cracking seen on the exposed face of irradiated samples (Figure 5) warrants further consideration. Since cracking is a response to strain brought about by shrinkage of the material [35, 36], the more extensive cracking indicates that irradiation has altered the mechanical properties of the cement matrix. On the microscale, cement is heterogeneous and this may lead to different radiation responses in different areas of the microstructure. The pore network usually consists of micro, meso and macropores (as defined by IUPAC) [40] which are filled with water and may not be interconnected: radiolysis of water in smaller pores leads to an increase in hydrogen production with an associated modification of the radiation chemistry [41, 42]. Cement also contains gel water which can be thought of as water between layers of C-S-H: Ca in the interlayer space can act as an electron trap, evidenced by enhanced radiolysis of the interlayer water [19]. Under irradiation, energy absorbed by a solid phase can be transferred to surface water and this

energy transfer is influenced by the chemistry of the solid [43]. More generally, irradiation of polymers is known to cause either cross-linking or chain scission (depending on the nature of the chemical bonds) which can affect mechanical properties [44, 45, 46]. Neutron irradiation has been shown to change the stored energy in many different materials [47], meaning it may be a possibility for a cementitious system. We can envisage a scenario where chemical bonds in the C-S-H are affected by irradiation but the exact response depends on local chemistry and local porosity. Differing amounts of strain may be responsible for the different crack patterns seen in Figure 5, and affect the crack depth seen in Figure 7.

4.2. Comparison to Carbonation Mechanisms Proposed in Other Studies

The formation of calcite in the irradiated samples contrasts with the results of Maruyama et al. [9] which found that irradiation induced the formation of vaterite and aragonite. The difference between the resultant polymorphs in our study and Maruyama et al. [9] is believed to be due to our study utilising FA blended cements, whereas Maruyama et al. [9] used solely OPC cements. Both our study and that of Maruyama et al. [9] showed that irradiation results in the formation of a different polymorph compared to carbonation alone. Maruyama et al. [9] gave advanced dehydration as the reason for this, and mentioned calcium peroxide octahydrate, produced as a result of radiolysis, as a possible pathway to forming vaterite. In our study, we can rule out the action of calcium peroxide octahydrate as it is unstable [21, 48] and declines quickly once the irradiation is halted, meaning the contribution in our sequential irradiation-then-carbonation study is negligible. Figure 9 shows that the samples exposed to heat treatment also

374 demonstrated a change in the dominant calcium carbonate polymorph, but
375 to a lesser extent compared to the irradiated sample, as shown by the maxi-
376 mum calcite: vaterite of 0.82 for the heat treated samples compared to 1.16
377 for the irradiated samples. This confirms that thermal dehydration is par-
378 tially responsible for the change in calcium carbonate polymorph switch,
379 however, the difference in the XRD results indicates that there must be an
380 additional process occurring in the irradiated samples. Since Figure 4 shows
381 the mass loss for both the irradiated and heat-treated samples ($3.71 \pm 0.47\%$
382 and $3.30 \pm 0.11\%$ respectively) after the treatment stage were within error,
383 this additional process cannot simply be due to water radiolysis leading to
384 further dehydration.

385 Auroy et al. [28] have shown that the different carbonate polymorphs have
386 different hydrated cement phase precursors: calcite was formed from port-
387 landite, aragonite was formed from ettringite and vaterite was formed from
388 C-S-H. Conversion of the precursor phases prior to carbonation is ruled out
389 by considering the sections of the XRD heatmaps in Figure 8 that are well
390 below the carbonation depth. Portlandite, C-S-H and quartz are all present
391 in the uncarbonated region. Another potential mechanism is the thermo-
392 dynamically driven vaterite to calcite transformation [25], which could be
393 accelerated by heat and/ or gamma irradiation. Rodriguez-Blanco et al. [25]
394 used synthesised calcium carbonates in an aqueous solution and observed
395 spherical indentations in the cubic calcite, which correlated to the nucleation
396 sites on the spherical vaterite particles. As shown in Figure 10, the calcite
397 particle did not feature a spherical indentation indicitive of a vaterite to
398 calcite transformation. Consequently, the calcite phase appear to be forming

399 from the pre-cursor phases directly, rather than the transforming through dif-
 400 ferent carbonation polymorphs. Figure 10 provides one more piece of infor-
 401 mation showing a somewhat imperfect morphology, rather than the perfectly
 402 cubic morphology of calcite, which is discussed in the next section.

403 *4.3. Evidence of Pore Water Chemistry Influencing Polymorph Formation*

404 The reason for vaterite forming in the control samples can also be ex-
 405 plored, with our results concurring with the findings of Auroy et al. [28],
 406 which showed vaterite to be the dominant calcium carbonate polymorph in
 407 fly-ash blended samples. Figure 11 shows a reduction of 52.14 μm 12.50% and
 408 $81.60 \pm 6.63\%$ for Na and K respectively elemental concentration at the
 409 carbonated edge of the material compared to the middle (non-carbonated)
 410 section. This implies that in the carbonated region of the cement samples
 411 Na and K are incorporated into an in-soluble solid phase, whereas in the
 412 non-carbonated area they are dissolved in the pore water.

413 Hofmann et al. [49] showed that Na^+ and K^+ ions adsorbing to the calcite
 414 surface destabilised the polymorph while Ishikawa and Ichikuni [50] calcu-
 415 lated that Na could sit in a calcite lattice as an interstitial atom alongside
 416 a Ca-vacancy. Other research utilising synthesised calcium carbonates has
 417 shown that the incorporation of ions such as S or Mg into the calcite lat-
 418 tice destabilises the polymorph [23, 24], with the inclusion of S leading to
 419 an increase in the c-axis [23]. A smaller change in the c-axis was observed
 420 for aragonite and there was no change for vaterite [23], meaning that these
 421 polymorphs are not destabilised by the inclusion of S and so are more sta-
 422 ble than S-containing calcite. We consider that a similar phenomenon may
 423 also be occurring for Na and K; interaction of these ions into the carbonate

424 lattice would explain the decrease in Na and K concentration in the leachate
425 at the carbonated edge. Na sitting within the carbonate lattice would result
426 in some Ca being removed from the calcium carbonate lattice, which would
427 explain the increased Ca content at the edge. Consequently, these authors
428 propose that incorporation of Na and K with the calcium carbonate lattice is
429 destabilising calcite and causing vaterite to become the dominant polymorph
430 in the control sample.

431 As shown by Figure 11, Mg isn't being leached in the non-carbonated
432 area and only a very small amount is observed in the carbonated edge. Con-
433 sequently, it appears that Mg is unlikely to be taking part in the solution
434 chemistry. There was a notable increase in the concentration of S in the
435 leachate from the carbonated edge of the sample, indicating that ettringite
436 carbonation has occurred [28, 38, 39].

437 The reason for the polymorph switch with gamma irradiation and or heat-
438 ing can also be explored. There is more carbonate formed in the irradiated
439 and heat treated samples compared to the control sample, as demonstrated
440 by Figure 6 and the mean carbonation ingresses provided in Table 2 showing
441 on average twice as much carbonation ingress for the heat treated and car-
442 bonated samples. Given that the uptake of Na and K is similar across all
443 three treatment methods, this suggests that the concentration of Na and K
444 in the carbonate phase is lower in the irradiated and heat treated samples.
445 The lower concentration of Na and K in carbonate phases for the irradiated
446 and heat treated samples cause less destabilisation and so make the forma-
447 tion of a more stable polymorph likely; this is why we also see calcite in
448 these samples. To the best of our knowledge a study has not been performed

449 that would determine the competing effects of these ions on calcite morphol-
450 ogy. In future work spectroscopic techniques such as x-ray photoelectron
451 spectroscopy (XPS) or nuclear magnetic resonance (NMR) can be used to
452 examine the structure of the carbonate phases.

453 The observed calcite crystal in Figure 10 was imperfect, supporting our
454 hypothesis that elements are substituting in and altering the crystal struc-
455 ture. Consequently, we believe that chemical processes, which are influenced
456 by the composition of the pore water, are also having an effect on the carbon-
457 ation product formation. As discussed previously, Na and K cations are less
458 concentrated in the carbonation phase for the irradiated and heated samples,
459 resulting in less destabilisation to the calcite phase, which explains why this
460 phase is observed. A dissolution of S is also observed in the centre of the
461 samples for both the irradiated and heated samples, however, the effect of
462 this is currently unknown. Literature has shown that amount of S in solution
463 alters the carbonation polymorph, with vaterite becoming more dominant at
464 higher S concentration [51, 25]. We are unable to tell if this is occurring in
465 our sample, given the other complex mechanisms that are happening simul-
466 taneously.

467 5. Conclusions

468 We have shown that the carbonation depth of samples increased when
469 the samples were pre-treated with either gamma irradiation or heat exposure
470 prior to accelerated carbonation. This is relevant to the nuclear industry, as
471 it shows increased carbonation depth is not limited to systems where the
472 radiation and carbonation occur simultaneously and could occur in systems

473 that experience a radiation field and then are exposed to the atmosphere,
474 like a nuclear waste storage facility maybe. Vaterite was observed as the
475 dominant carbonation phase in the control sample. We propose the vaterite
476 formation is due to the pore water chemistry, in-particular the Na and K ions
477 being either incorporated into the calcite lattice or adsorbing onto the surface,
478 de-stabilising the calcite polymorph. A switch in the carbonation phase from
479 vaterite to calcite was observed with gamma irradiation or heating prior to
480 carbonation, with gamma irradiation having more substantial effect than
481 heating alone. The polymorph formed in carbonation is important for the
482 nuclear industry to know as the different molar volumes affect the porosity
483 differently and could lead to a different timescale for the self termination of
484 the carbonate reaction. The use of a sequential process infers that the calcium
485 peroxide octahydrate does not play a significant part in the carbonation or
486 the carbonation product switch due to it being highly unstable.

487 A definite mechanism behind the carbonation product switch remains un-
488 clear, however, currently our results concur with the literature that advanced
489 dehydration being a factor. These authors also propose that chemical pro-
490 cesses are also influencing the switch in carbonation phase, as demonstrated
491 by the pore water data. We propose that the gamma irradiation is acceler-
492 ating these processes, rather than creating a separate mechanism, resulting
493 in the larger calcite:vaterite ratio.

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511 7. References

512 References

- 513 [1] D. Naus, Primer on Durability of Nuclear Power Plant Reinforced Con-
514 crete Structures - A Review of Pertinent Factors Primer on Durability
515 of Nuclear Power Plant Reinforced Concrete Structures - A Review of
516 Pertinent Factors, Technical Report, Oak Ridge National Laboratory,
517 2006.
- 518 [2] W. Ashraf, Carbonation of cement-based materials: Challenges and
519 opportunities, *Construction and Building Materials* 120 (2016) 558–570.
- 520 [3] B. Šavija, M. Luković, Carbonation of cement paste: Understanding,
521 challenges, and opportunities, *Construction and Building Materials* 117
522 (2016) 285–301.
- 523 [4] S. Hussain, D. Bhunia, S. B. Singh, Comparative study of accelerated
524 carbonation of plain cement and fly-ash concrete, *Journal of Building*
525 *Engineering* 10 (2017) 26–31.
- 526 [5] H. Taylor, *Cement Chemistry*, Thomas Telford Publishing, second edi-
527 tion, 1997.
- 528 [6] C. D. Atiş, Accelerated carbonation and testing of concrete made with
529 fly ash, *Construction and Building Materials* 17 (2003) 147–152.
- 530 [7] M. Stefanoni, U. Angst, B. Elsener, Corrosion rate of carbon steel in
531 carbonated concrete – A critical review, *Cement and Concrete Research*
532 103 (2018) 35–48.

- 533 [8] S. Ahmad, Reinforcement corrosion in concrete structures, its mon-
534 itoring and service life prediction - A review, Cement and Concrete
535 Composites 25 (2003) 459–471.
- 536 [9] I. Maruyama, S. Ishikawa, J. Yasukouchi, S. Sawada, R. Kurihara,
537 Impact of gamma-ray irradiation on hardened white portland cement
538 pastes exposed to atmosphere, Cement and Concrete Research 108
539 (2018) 59–71.
- 540 [10] F. Vodák, V. Vydra, K. Trtík, O. Kapičková, Effect of gamma irradiation
541 on properties of hardened cement paste, Materials and Structures
542 44 (2011) 101–107.
- 543 [11] G. Bar-Nes, A. Katz, Y. Peled, Y. Zeiri, The combined effect of radiation
544 and carbonation on the immobilization of Sr and Cs ions in cementitious
545 pastes, Materials and Structures 41 (2008) 1563–1570.
- 546 [12] H. Hilsdorf, J. Kropp, H. Koch, The Effects of Nuclear Radiation on Ma-
547 terials, Technical Report 4, Institute for Building Materials, University
548 of Karlsruhe, 1959.
- 549 [13] F. Vodák, K. Trtík, V. Sopko, O. Kapičková, P. Demo, Effect of γ -
550 irradiation on strength of concrete for nuclear-safety structures, Cement
551 and Concrete Research 35 (2005) 1447–1451.
- 552 [14] P. Soo, L. Milian, The effect of gamma radiation on the strength of
553 Portland cement mortars, Journal of materials science letters 20 (2001)
554 1345–1348.

- 555 [15] N. Mobasher, S. a. Bernal, H. Kinoshita, C. a. Sharrad, J. L. Provis,
556 Gamma irradiation resistance of an early age slag-blended cement matrix
557 for nuclear waste encapsulation, *Journal of Materials Research* (2015)
558 1–9.
- 559 [16] B. Craeye, G. De Schutter, C. Vuye, I. Gerardy, Cement-waste interac-
560 tions: Hardening self-compacting mortar exposed to gamma radiation,
561 *Progress in Nuclear Energy* 83 (2015) 212–219.
- 562 [17] E. Tajuelo Rodriguez, W. A. Hunnicutt, P. Mondal, Y. Le Pape, Exami-
563 nation of gamma-irradiated calcium silicate hydrates. Part I: Chemical-
564 structural properties, *Journal of the American Ceramic Society* 103
565 (2020) 558–568.
- 566 [18] F. Chupin, A. Dannoux-Papin, Y. Ngono Ravache, J. B. d’Espinose de
567 Lacaille, Water content and porosity effect on hydrogen radiolytic
568 yields of geopolymers, *Journal of Nuclear Materials* 494 (2017) 138–
569 146.
- 570 [19] S. Le Caër, L. Dezerald, K. Boukari, M. Lainé, S. Taupin, R. M. Ka-
571 vanagh, C. S. Johnston, E. Foy, T. Charpentier, K. J. Krakowiak, R. J.
572 Pellenq, F. J. Ulm, G. A. Tribello, J. Kohanoff, A. Saúl, Production
573 of H₂ by water radiolysis in cement paste under electron irradiation:
574 A joint experimental and theoretical study, *Cement and Concrete Re-*
575 *search* 100 (2017) 110–118.
- 576 [20] O. Kontani, S. Sawada, I. Maruyama, M. Takizawa, O. Sato, Evaluation
577 of Irradiation Effects on Concrete Structure - Gamma Ray Irradiation

- 578 Tests on Cement Paste -, in: Proceedings of the ASME 2013 Power
579 Conference, pp. 1–8.
- 580 [21] P. Bouniol, E. Bjergbakke, A comprehensive model to describe radiolytic
581 processes in cement medium, *Journal of Nuclear Materials* 372 (2008)
582 1–15.
- 583 [22] M. Ni, B. D. Ratner, J. Wiley, Differentiating calcium carbonate poly-
584 morphs by surface analysis techniques – an XPS and TOF-SIMS study,
585 *Surface & Interface Analysis* 40 (2008) 1356–1361.
- 586 [23] P. Bots, L. G. Benning, R. E. Rickaby, S. Shaw, The role of SO₄ in the
587 switch from calcite to aragonite seas, *Geology* 39 (2011) 331–334.
- 588 [24] J. W. Morse, Q. Wang, M. Y. Tsio, Influences of temperature and
589 Mg:Ca ratio on CaCO₃ precipitates from seawater, *Geology* 25 (1997)
590 85–87.
- 591 [25] J. D. Rodriguez-Blanco, S. Shaw, L. G. Benning, The kinetics and
592 mechanisms of amorphous calcium carbonate (ACC) crystallization to
593 calcite, via vaterite., *Nanoscale* 3 (2011) 265–271.
- 594 [26] J. D. Rodriguez-Blanco, S. Shaw, P. Bots, T. Roncal-Herrero, L. G.
595 Benning, The role of pH and Mg on the stability and crystallization of
596 amorphous calcium carbonate, *Journal of Alloys and Compounds* 536
597 (2012) S477–S479.
- 598 [27] M. Castellote, L. Fernandez, C. Andrade, C. Alonso, Chemical changes
599 and phase analysis of OPC pastes carbonated at different CO₂ concen-
600 trations, *Materials and Structures* 42 (2009) 515–525.

- 601 [28] M. Auroy, S. Poyet, P. Le Bescop, J. M. Torrenti, T. Charpentier,
602 M. Moskura, X. Bourbon, Comparison between natural and accelerated
603 carbonation (3% CO₂): Impact on mineralogy, microstructure, water
604 retention and cracking, *Cement and Concrete Research* 109 (2018) 64–
605 80.
- 606 [29] Y.-H. Hsiao, B. Wang, E. Callagon, L. Plante, I. Pignatelli, N. M. A.
607 Krishnan, The effect of irradiation on the atomic structure and chemical
608 durability of calcite and dolomite, *npj Materials Degradation* (2019) 1–
609 9.
- 610 [30] B. Pomaro, A review on radiation damage in concrete for nuclear fa-
611 cilities: From experiments to modeling, *Modelling and Simulation in*
612 *Engineering* (2016) 1–10.
- 613 [31] K. Field, I. Remec, Y. Le Pape, Radiation effects in concrete for nuclear
614 power plants - Part I: Quantification of radiation exposure and radiation
615 effects, *Nuclear Engineering and Design* 282 (2015) 126–143.
- 616 [32] BS EN 197-1:2011, Cement. Composition, specifications and conformity
617 criteria for common cements, Standard, British Standards Institution,
618 2011.
- 619 [33] BS EN 450-2:2005, Fly ash for concrete. Conformity evaluation, Stan-
620 dard, British Standards Institution, 2005.
- 621 [34] L. Leay, W. Bower, G. Horne, P. Wady, A. Baidak, M. Pottinger,
622 M. Nancekievill, A. D. Smith, S. Watson, P. R. Green, B. Lennox, J. A.

- 623 Laverne, S. M. Pimblott, Development of irradiation capabilities to ad-
624 dress the challenges of the nuclear industry, Nuclear Instruments and
625 Methods in Physics Research, Section B: Beam Interactions with Mate-
626 rials and Atoms 343 (2015) 62–69.
- 627 [35] W. Hansen, Drying Shrinkage Mechanisms in Portland Cement Paste,
628 Journal of the American Ceramic Society 70 (1987) 323–328.
- 629 [36] I. Maruyama, Origin of drying shrinkage of hardened cement paste:
630 Hydration pressure, Journal of Advanced Concrete Technology 8 (2010)
631 187–200.
- 632 [37] L. De Ceukelaire, D. Van Nieuwenburg, Accelerated carbonation of a
633 blast-furnace cement concrete, Cement and Concrete Research 23 (1993)
634 442–452.
- 635 [38] D. Zhang, D. Xu, X. Cheng, W. Chen, Carbonation resistance of
636 sulphoaluminate cement-based high performance concrete, Journal
637 Wuhan University of Technology, Materials Science Edition 24 (2009)
638 663–666.
- 639 [39] L. Fernández-Carrasco, D. Torrén-Martín, S. Martínez-Ramírez, Car-
640 bonation of ternary building cementing materials, Cement and Concrete
641 Composites 34 (2012) 1180–1186.
- 642 [40] M. Thommes, K. Kaneko, A. V. Neimark, J. P. Olivier, F. Rodriguez-
643 Reinoso, J. Rouquerol, K. S. Sing, Physisorption of gases, with special
644 reference to the evaluation of surface area and pore size distribution

- (IUPAC Technical Report), *Pure and Applied Chemistry* 87 (2015) 1051–1069.
- [41] S. Le Caër, P. Rotureau, F. Brunet, T. Charpentier, G. Blain, J. P. Renault, J. C. Mialocq, Radiolysis of confined water: Hydrogen production at a high dose rate, *ChemPhysChem* 6 (2005) 2585–2596.
- [42] P. Rotureau, J. P. Renault, B. Lebeau, J. Patarin, J. C. Mialocq, Radiolysis of confined water: Molecular hydrogen formation, *ChemPhysChem* 6 (2005) 1316–1323.
- [43] N. G. Petrik, A. B. Alexandrov, A. I. Vall, Interracial energy transfer during gamma radiolysis of water on the surface of ZrO₂ and some other oxides, *Journal of Physical Chemistry B* 105 (2001) 5935–5944.
- [44] E. Craven, F. Hasanain, M. Winters, Minimizing material damage using low temperature irradiation, *Radiation Physics and Chemistry* 81 (2012) 1254–1258.
- [45] S. Shaffer, K. Yang, J. Vargas, M. A. Di Prima, W. Voit, On reducing anisotropy in 3D printed polymers via ionizing radiation, *Polymer* 55 (2014) 5969–5979.
- [46] P. Wady, A. Wasilewski, L. Brock, R. Edge, A. Baidak, C. McBride, L. Leay, A. Griffiths, C. Vallés, Effect of ionising radiation on the mechanical and structural properties of 3D printed plastics, *Additive Manufacturing* 31 (2020) 100907.
- [47] L. L. Snead, Y. Katoh, T. Koyanagi, K. Terrani, Stored energy release

- 667 in neutron irradiated silicon carbide, *Journal of Nuclear Materials* 514
668 (2019) 181–188.
- 669 [48] P. Bouniol, Disappearance of Oxygen in Concrete Under Irradiation:
670 the Role of Peroxides in Radiolysis, *Cement and concrete research* 28
671 (1998) 1669–1681.
- 672 [49] S. Hofmann, K. Voitchovsky, P. Spijker, M. Schmidt, T. Stumpf, Visu-
673 alising the molecular alteration of the calcite (104) - Water interface by
674 sodium nitrate, *Scientific Reports* 6 (2016) 1–11.
- 675 [50] M. Ishikawa, M. Ichikuni, A Model of Crystal Defects in Calcite by
676 Sodium and Potassium Uptake, *Bulletin of the Chemical Society of*
677 *Japan* 59 (1986) 3809–3814.
- 678 [51] I. C. Mayorga, J. M. Astilleros, L. Fernández-Díaz, Precipitation of
679 caco 3 polymorphs from aqueous solutions: The role of ph and sulphate
680 groups, *Minerals* 9 (2019) 1–16.